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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Sintered Porous Metallic Material and method of making it

We, GENERAL ELECTRIC COMPANY, a Corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a sintered porous metallic material of controllable uniform porosity and density and to a method for making same.

Porous metals or metals including intentional cavities, pores or voids made by methods prior to this invention do not possess the uniformity of porosity and density required in many of today's applications. From uses such as in closely balanced seals for power producing apparatus to uses in chemical processes involving control of fluid flow, more rigid requirements are being specified for porous metal than could be satisfied prior to this invention.

An object of this invention is to provide a porous metallic material the density and porosity of which can accurately be controlled.

In accordance with this invention there is provided a method of preparing a porous metal comprising the steps of mixing a metallic powder, hollow microspherical particles of an organic resinous material, and a hardenable organic binder, curing the mixture to produce a hardened form, heating said form to decompose and remove the organic materials, and finally heating the form to a temperature sufficient to sinter the metallic particles to one another to result in a porous metallic body substantially free from organic materials.

In the preparation of the present porous metallic material, it is best to thoroughly mix the dry metallic powder and dry hollow microspherical organic particles prior to introducing them into a liquid resin or mixture of resins which subsequently act as a binder for the dry

mix. However, if such binder resins are initially in dry rather than liquid form, a mixture of all such dry materials can be made.

The final product of this invention consists essentially of a porous metal body with substantially no residue products from the organic components used in the process.

For the process, it is preferred that a fine metallic powder of a particle size of 0.044mm diameter comprising 20%-95% by weight of the total mixture be blended with 1%-25% by weight of the total mixture of organic particles of generally spherical shape (microspheres) which have been previously classified according to size by standard particle classifying means such as screens and air classifiers, and which preferably have a particle size within the range 5-20 microns.

After the two dry materials have been thoroughly mixed, it is preferred that they be added to a hardenable organic binder resin or mixture of resins which comprises 5%-55% by weight of the total mix.

The resulting mixture of metal powder, microspheres and binder is then placed in a mold and cured. Some binder materials require heating to cure such as within the temperature range of 120°C-260°C for at least 10 minutes. Others will air harden or can be catalyzed to harden at room temperatures.

After an initial cure has taken place, the green material is then pre-sintered or preliminarily bonded by heating to decompose the organic microspheres and organic binding resins within the temperature range of 455°C-650°C. Usually at least 40 minutes is required. Even if the type of metal powder used makes it desirable or necessary that the decomposition heating step be conducted in a non-oxidizing atmosphere such as a vacuum or a reducing atmosphere, an additional heat treatment in an oxidizing atmosphere such as air between 370°C-816°C is necessary to remove the carbon deposits or residues remaining from the decomposition of the organic

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- ingredients. In this case the oxidizing atmosphere and the additional heat treatment must be carefully controlled to prevent or minimise as far as possible oxidation of the metal itself.
- 5 The porous material is then heated at a relatively high temperature generally for at least 40 minutes and preferably in a vacuum or reducing atmosphere to a temperature sufficient to sinter and to further bond the metallic powder or powders. Thus there is formed a controlled density metallic product. The only limitation on the type of metallic powders which can be used in the method and product of this invention is that the melting point of the metal be at least 28°C above the decomposition temperature of the organic ingredients used. Therefore, refractory metals such as tungsten, molybdenum, columbium and their alloys can be incorporated as metallic powders in the method and product of this invention. In such cases the maximum sintering temperature of the powders is 28°C below the melting point of such metals or alloys. In addition, lower melting metallic powders can be included in a metallic powder mix to allow liquid phase sintering techniques to be used to bind the powders together as well as to afford a means to make controlled alloys through mixtures of elemental or alloy powders.
- 10 The examples of the following Table I are representative of the range of the method and products of this invention.
- 15 20 25 30

TABLE I

Example	% Density*	Type Metal Powder	Metal Powder	% BY WEIGHT		
				Hollow Phenolic Micro-spheres	Acrylic Resin (20% Solids)	Phenolic Resin
1	15	Ni	53.3	14.7	24.0	8.0
2	18	Ni	58.0	13.0	21.7	7.3
3	20	Ni	60.7	12.2	20.3	6.8
4	25	Ni	66.8	10.0	17.4	5.8
5	50	Ni	80.0	5.6	10.8	3.6
6	85	Ni	87.8	2.9	7.0	2.3
7	15	Au	74.6	7.9	13.1	4.4
8	85	Au	94.1	1.4	3.4	1.1
9	15	Mg	21.6	24.3	40.6	13.5
10	85	Mg	63.2	8.7	21.0	7.1

*based on solid metal of the same composition and volumes as 100% density.

In the examples 1-10 of Table I the hollow microspheres used were made from phenol-formaldehyde resin and had a diameter of 5-20 microns. The binder resins in those examples were a mixture of a 20% solids solution of acrylic resin monomeric methyl methacrylate in toluol and a liquid phenol-formaldehyde resin of the Novolac type.

The procedure used in the preparation of the porous metals of examples 1-6 is as follows; the method for examples 7-10 and other metals as discussed herein differ only in the temperature and times of heating as indicated by representative examples in Table II herein.

The nickel powder and hollow phenolic microspheres were blended in a shell blender for about 30 minutes.

After such separate blending and mixing steps were complete, the dry ingredient blend was slowly mixed with the liquid resin mixture until a sticky, slightly moist paste formed. The moist paste was then placed in a mold shell then covered and placed in a heated press at about 173°C where it was held for about 1 hour.

The resulting solidified body (green form) was held at from 482°C-593°C for 1 hour to decompose the organic ingredients.

Thereafter, the molded piece was then

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heated to and held at 1200°C for about 1½ hours. It was then removed and placed in a furnace with an oxidizing (air) atmosphere at about 650°C for one hour which was sufficient to oxidize substantially all the carbon to a gaseous oxide form and evolve it.

The resulting carbon-free molded piece was placed in a hydrogen furnace for final sintering at 1200°C-1343°C for about an hour and a half after which it was cooled in hydrogen before removing to the atmosphere. The final sintering step improved the bond strength and the ductility of the final product.

If desired, rather than varying the compositions of the various materials as listed in Table I, a moist paste such as that which

in Example 2 would result in a product having a density of 18% of the density (approximately 1.6 grams per cubic centimeter) of solid nickel of the same volume, can be sized and pressed while still moist to result in a product having any desired density above 18%. In such a case the uniformity of porosity is substantially maintained with only the size or shape of openings being changed.

The following Table II represents the heat treatment cycle found to be useful in connection with the various materials listed therein. The organic material decomposition step for all of the materials listed in Table II include a temperature of 482°C—593°C for 1 hour:

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TABLE II

Powdered Material	Presinter	Oxidation	Sinter	
	Temp. (°C) for 1 hour	Temp. (°C) for 1 hour	Temp (°C)	Time (hrs)
Al	593	482	593	1.5
Cu	1010	593	1010	"
Au	982	593	982	"
Fe	1093	649	1288	"
Mg	593	482	593	"
Ni	1200	649	1343	"
Pt	1232	649	1639	"
Ag	871	538	871	"
95 Cu - 5 Sn	843	538	843	"
80 Cu - 20 Sn	760	538	760	"
90 Cu - 10 Zn	982	593	982	"
80 Cu - 20 Zn	927	593	927	"
90 Cu - 5 Sn - 5 Zn	982	593	982	"
70 Cu - 10 Sn - 20 Zn	704	482	704	"
70 Cu - 20 Sn - 10 Zn	760	538	760	"
50 Ni - 50 Al	1232	649	1260	3
75 Ni - 25 Al	1232	649	1482	3

Although the examples above show the binder resin to be a combination of phenolic and acrylic resins, it has been found that acrylic resin or phenolic resin alone can be used

equally as well as the mixture of resins. In addition, other hardenable resins such as of the epoxy condensation product of bisphenol A and epichlorohydrin or silicone (methyl phenyl

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silane) types can be used. In addition, hollow microspheres of other organic materials, which can be removed by heating, can be substituted for the phenolic microspheres.

- 5 Thus, through the elimination of such constituents as blowing agents, chemical reactive materials to produce gases, air intermixed in the constituents, etc., this invention provides a uniformly porous material of easily controlled
10 density.

WHAT WE CLAIM IS:—

- 15 1. A method of preparing a porous metal comprising the steps of mixing a metallic powder, hollow microspherical particles of an organic resinous material, and a hardenable organic binder, curing the mixture to produce a hardened form, heating said form to decompose and remove the organic materials, and finally heating the form to a temperature sufficient to sinter the metallic particles to one another to result in a porous metallic body substantially free from organic materials.
20 2. A method as claimed in claim 1, in which the mix comprises by weight 1%—25% hollow microspherical organic particles, 20%—95% metallic powder, and 5%—55% organic binder.
25 3. A method as claimed in claim 1, in which the organic binder is a phenolic resin.
30 4. A method as claimed in claim 1, in which the organic binder is a mixture of phenolic and acrylic resins.
35 5. A method as claimed in any preceding

claim, comprising the steps of blending 1%—25% by weight of hollow spherically shaped phenolic particles within the size range of 5—20 microns diameter with 20%—95% by weight of a metallic powder; mixing the blend with 5%—55% by weight of liquid organic binder the percentages being based on the total weight of the mix; curing the mix to produce a hardened form; heating the form in a non-oxidizing atmosphere at 455°C—650°C to decompose the organic particles and organic resin and to preliminarily bond the metallic powder together; heating the form in an oxidizing atmosphere at 370°C—816°C to remove from the form carbon residue remaining from the decomposition of the organic ingredients; and then heating the form at a sintering temperature which is no higher than 28°C below the melting point of the metallic powder to further bond together the metallic powder.

40 6. A method of preparing a porous metal substantially as hereinbefore described in any one of the foregoing Examples.

45 7. A porous metallic material prepared by the method claimed in any preceding claim and having a density of 15%—85% of the solid metal of the same composition and volume.

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